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14. ABSTRACT This research focuses on the nanoscale control of matrix morphology through void and particle introduction. The main areas of research have been the study of interlayer modification of composites at the nanoscale, improvement of the damage tolerance of carbon fiber reinforced laminates with epoxy foam and nanoparticles, and VARTM processing of nanoclay filled composites. The results showed improvement in toughness up to a critical threshold after which an increase in the concentration of nanoparticulate montmorillonite clay in the matrix deteriorated fracture toughness properties significantly. Furthermore, nanoscale clays could be used after the response of composite materials to a hygrothermal environment. The results also indicated that the presence of a foam interlayer enhanced specific composites fracture toughness in relation to weight.				
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FINAL PERFORMANCE REPORT

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NANO-PARTICLE CONTROL OF VOID FORMATION AND EXPANSION IN  
POLYMERIC AND COMPOSITE SYSTEMS

AFOSR Grant No. FA9550-04-1-0157

Submitted to

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## AFOSR 2004-2005 Final Report

### **Executive Summary:**

The research focused on carbon fiber reinforced epoxy composites with varying dispersions of montmorillonite and nanoprocity, processed with either prepreg or Vacuum Resin Transfer Mold (VARTM) technologies. The most significant advancements and conclusions in this final report include interlayer modification of composites at the nanoscale and characterization of the interlayer behaviour of nanoparticles and nanoporous composites, as well as VARTM processing of nanoclay filled composites.

### **Status of Effort:**

The application of polynanomer concepts to traditional continuous fiber reinforced composites has seen only limited research thus far. In particular, the interlaminar fracture response of these materials shows considerable promise for utilization. Both nanoscale particulates and nanoscale voids have been introduced into the matrix of traditional fiber reinforced composites to determine their influence on fracture behavior.

It has been demonstrated that a very low concentration of nanoparticulate montmorillonite clay in the matrix greatly enhances fracture toughness. However, as concentration is increased, a critical threshold is reached, beyond which fracture toughness decreases significantly with increased particle loading. This change represents a radically different fracture mechanism between high and low clay loading scenarios. This difference is attributed to a change in particle dispersion morphology. In order to gain a fundamental understanding of these morphological effects, attempts are being made to vary particle dispersion under fixed concentration and fixed material system conditions. It is believed that this will clarify the role of different morphologies, without the commingling of data presented by altering clay and resin chemistry.

The effects of introducing voids into the matrix have also provided interesting insight into the interlaminar fracture of composites. The morphology of the introduced voids was controlled by altering matrix processing and formulation conditions. In

general, microcellular foam technology has demonstrated that substantially improved specific mechanical properties are possible versus to traditional cellular materials. Thus far, we demonstrated that the introduction of nano and microscale voids may be used to reduce matrix density without adversely affecting mode I fracture toughness. However, the introduction of voids has been shown to significantly decrease mode II fracture toughness. Continued work on reducing cell size and improving size dispersity should lead to a more thorough understanding of the prospects for viable cellular matrices.

The research during the past year focused on carbon fiber reinforced epoxy composites with varying dispersions of montmorillonite and nanoporosity, processed with either prepreg or Vacuum Resin Transfer Mold (VARTM) technologies. The most significant advancements and conclusions in this report include interlayer modification of composites at the nanoscale and characterization of the interlayer behaviour of nanoparticles and nanoporous composites, as well as VARTM processing of nanoclay filled composites.

The research focused on the investigation of nanoparticle control of void formation and expansion in polymeric and composite systems. The main areas of the research have been the study of the montmorillonite reinforced carbon fiber epoxy composites and the improvement of the damage tolerance of carbon fiber reinforced laminates using epoxy foam interlayer.

One key area of interest has been the use of montmorillonite to improve the barrier properties of a given material. In this research, organically modified montmorillonite was incorporated into carbon fiber reinforced epoxy composites as a means of effecting the change in material properties resulting from hygrothermal exposure. Montmorillonite has been incorporated into the composites in the bulk resin, as well as the interlayer region using a double pass impregnation. Intercalated montmorillonite was shown to dramatically affect the response of materials subjected to hygrothermal exposure, particularly when applied at the interlayer.

Moreover, previous research showed that carbon fiber reinforced laminates with an epoxy foam interlayer showed improved damage tolerance. In this work, the effects of different process parameters such as foaming and curing conditions as well as chemical

reactant types on the morphology and mechanical properties of carbon fiber reinforced epoxy foam laminates were investigated.

In the past two decades, a considerable amount of polymer composite research has shifted towards the study of materials whose heterogeneities are defined at the nanometer scale. These materials often exhibit material properties not predicted by classical rule of mixtures type equations. The behavior of these materials becomes defined by unique polymer interactions in the vicinity of solid and gaseous surfaces. Unlike traditional micro-scale composites, nanocomposites have sufficient surface area that these interfacial phenomena begin to affect bulk behaviors. Material properties that blur traditional material and size classification have led to the coining of the concepts of polyanomers, polyanomeric composites, and polyanomatrix continuous fiber reinforced composites.

#### **Accomplishments/New Findings:**

In this study, carbon fiber reinforced epoxy composites with varying amounts and dispersions of montmorillonite were exposed to a high temperature-high humidity environment for a number of days. It has been reported by Becker et al. that the presence of montmorillonite in neat epoxy resin reduces the equilibrium water uptake of the material. Therefore, it was desired to take advantage of this improved barrier resistance to produce more consistent mechanical properties in composites exposed to harsh environments. Todo et al. showed that moisture had a pronounced effect on the mode II fracture of carbon/epoxy composites. This suggested that by controlling moisture ingress in the composite, other critical mechanical properties might also be controlled.

Composites have been produced through prepreg processing that employs both single and double pass impregnation techniques. It was desired to create samples with montmorillonite well distributed in the bulk resin, as well as samples where the particles were maintained predominantly in the interlayer region. Interlayer modification proved to be an effective means of locally toughening composite materials by creating a resin rich area with properties differing from the bulk material. Additionally, interlayer modification helped prevent some fouling of the fiber matrix interface, fouling that might

have reduced properties such as strength. Interlayer and bulk modified specimens were produced and exposed to an 85°C, 95% humidity environment for up to 9 days. After exposure, the effects of the warm moist environment on mode II fracture and dynamic mechanical response was evaluated.

Organically modified montmorillonite was shown to have dramatic effects on the properties of carbon fiber reinforced composites exposed to a strong hygrothermal environment. Particularly when incorporated in the composite interlayer, montmorillonite was shown to aid in the toughening of composites. When exposed to a high humidity and moderate temperature, layered silicate nano-composites alter their glass transition behavior into a lower temperature phase. Particularly in resin rich interlayer composites, this has resulted in a large increase in fracture toughness. Overall, it was shown that nano-scale clays could be used to alter the response of composite materials to a hygrothermal environment. Furthermore it was demonstrated that layered silicates may be dispersed in the composite in either the bulk or interlayer regions, with each providing specific changes to the material.

The unique nanomorphology of montmorillonite modified polymer systems has been shown to dramatically modify certain critical properties of the resultant material system. In this study, organically modified montmorillonite was incorporated into carbon fiber reinforced epoxy composites and a number of montmorillonite modified epoxy systems were made. The results showed the presence of a tactoidal structure, meaning that no swelling of the clay platelet gallery had occurred. In the case of an intercalated nanocomposite, it was found that the polymer had penetrated the individual clay platelets, causing swelling of the gallery region. In conclusion, the interlayer modified systems contained a continuum of morphologies from intercalation at the resin rich side to exfoliation in the diffused particles on the unmodified side. The fracture toughness results indicated that the incorporation of interlayer montmorillonite was an effective means of generating localized resin rich areas with improved fracture toughness.

Furthermore, dynamic mechanical analysis was used as a direct means to measure matrix plasticization. The glass transition behavior of the composite gives an indication of the polymer molecules' ability to undergo molecular movement. The presence of moisture in the polymer acts as molecular ball bearings, allowing larger scale molecular

movements with lower energy input. It was proposed that moisture accumulated at the hydrophilic clay and created local highly plasticized regions with transition behavior differing from the bulk. Taking direct advantage of this discrete plasticization may provide a future means of toughening composite materials.

The mechanism of exfoliation in layered silicate - epoxy nanocomposites was investigated using ex-situ x-ray diffraction (XRD) measurements taken during dynamic and isothermal curing cycles. Cure temperature ranges were determined by DSC to coincide with the termination of the exotherm peak observed during cure. During cure, samples were sequentially removed from the heating system and immediately quenched to slow the polymerization reaction and lock-in the layered silicate morphology. The quenched samples were exposed to XRD analysis so that silicate d-spacing was determined as a function of cure advancement. The changes in silicate morphology were correlated to the thermal events measured using DSC. Ultimately, this approach will be used to develop specific cure cycles to control and optimize the properties of montmorillonite filled nanocomposites. By varying the polymerization conditions of an in-situ polymerized epoxy - layered silicate nanocomposite, the resultant morphology was directly influenced. To explain this phenomenon, other researchers have proposed that an increased rate of intragallery polymerization is responsible for affecting the morphology at different cure temperatures. We demonstrated that cure rate, as well as cure temperature, can be used to elicit some control over final morphology. In general it was shown that higher heating rate and lower cure temperatures resulted in the least ordered morphology. The work in progress includes using the B-staging reaction to control the molecular length of the diffusing species for allowing greater control of intergallery chemistry by controlling the diffusion rate.

The effects of the addition of various types of nanoclay on the properties of epoxy/clay nanocomposites were investigated. Three types of modified organoclay were incorporated into VARTM resins at various concentrations. A Rheometric Dynamic Analyzer was used to analyze the flow behavior of the resins, while the morphology of the clay was examined by XRD and Transmission Electron Microscope (TEM). The

results indicated that the viscosity of the resins increased after the addition of the clays and the clays were exfoliated into the matrix. This increase in viscosity had no significant effect on the infusion process. The nanoclay was generally well dispersed into the matrix with areas of good exfoliated morphology. Nanoclay type did not influence the morphological or the rheological properties.

At present, carbon fiber-reinforced plastics (CFRP) are being incorporated into various products from aerospace to sporting goods. CFRPs possess different properties depending on the type of matrix being used. Changing the matrix type can also alter the properties of the epoxy with carbon fibers. One such alteration is a decrease in weight when the matrix is changed from epoxy to epoxy foams. Epoxy foams with the carbon fibers are seldom used for mechanical applications, as they are considered weak materials. However, it is possible to modify the properties of these foams if the size of the pores were controlled at nanoscale. In this research, porous foams were prepared and the size of the pores was controlled at nanoscale. The foam samples were obtained through using various amounts of styrene oxide at different processing conditions. The thermophysical, morphological and mechanical properties of the nanoe epoxy foams with carbon fiber were investigated.

The morphological studies showed that the stirring rate and time, foaming agent content and surfactant content had no significant effect on the foam size. The styrene oxide content and the pressure considerably influenced the size of the foams. The decrease in the styrene oxide content and increase of pressure led to the decrease of foam size, indicating that foam size can be controlled at the nanoscale. However, the difference in foam morphology was not sufficient enough to suggest that formation of foam affect the mechanical properties such as  $G_{Ic}$  and  $G_{IIc}$ . The presence of foam in the samples decreased the fracture toughness values. Further work on the precise control of the nanofoam size through optimization of the processing conditions is under investigation.

Details of these findings may be obtained from the listed papers cited at the reference section of this report.



## **NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES**

None, as Prof. Seferis takes no patents either personally or through the University. All his work is published in the open literature, and he works with companies that implement his work in products and processes.

### **Personnel Supported:**

#### **Faculty:**

Professor James C. Seferis

#### **Post-Doctoral Fellow:**

Dr. Samra S. Sangari

#### **Graduate Students:**

Mr. Jason Killgore

Ms. Kyoko Ishiguru

#### **Other researchers:**

Ms. Misaki Takemori

### **Publications:**

1. Lu, L., Georgoulis, L., Seferis, J. C., Komninelli, C., Andrianopoulos, N., Lawrence, W., Aardahl, C., Morgan, M., and Nam, J.D., "Nanogravimetric Processing of Polymeric Composites for High Temperature Filtration", Proceedings of the 11<sup>th</sup> European Conference on Composite Materials, Rhodes, Greece, May31-June 3 (2004), Accepted.
2. Seferis, J. C., "Thermal Characterization of Polymers, Nanomers, and Polynanomers", 13<sup>th</sup> International Confederation for Thermal Analysis and Calorimetry, Sardinia, Italy, September 12-19 (2004), Accepted.
3. Ishiguro, K. Karaki, T. Sangari, S.S. and Seferis, J.C., "Epoxy Foams for Polynanomeric Reinforced Composites", Society for the Advancement of Material and Process Engineering (SAMPE) 2004 Symposium and Exhibition, San Diego, CA, November 15-18, (2004), Accepted.

4. Killgore, J.P., Jensen, T., Peila, R., Sangari, S.S. and Seferis, J.C., "Assessment of Durability in High Performance Polymeric and Polynanömeric Matrix Composites", Society for the Advancement of Material and Process Engineering (SAMPE) 2004 Symposium and Exhibition, San Diego, CA, November 15-18, (2004), Accept
5. Seferis J.C., "Polynanömeric Composites: A Novel Concept for Polymeric Composites Systems", 7th Mediterranean Conference on Calorimetry and Thermal Analysis (MEDICTA 2005), 2-6 July, Thessaloniki, Greece, (2005).
6. Nam, J.D., Lee, Y., Cho, S.M., Jung, C.H. Choi, H.G., Jang, Y.Y., Kwon, Y.U., Nam, J.H., Seferis, J.C., "Nanocomposites and Nanoreplication Techniques in Direct Methanol Fuel Cell", Asia/NANO 2004, Beijing, China, November 24-27, (2004).
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10. Peila R., Sangari S. S., Karaky T., Seferis J. C. and Parker G., "Rheological and Morphological Properties of VARTM (Vacuum Assisted Resin Transfer Molding) Epoxy Resin/ Clay Nanocomposites", Society of Plastics Engineering (SPE) 2005 Annual Technical Conference (ANTEC), Boston, Massachusetts, May 1-5 (2005).
11. Ishiguro, K. Karaki, T. Sangari, S.S. and Seferis, J.C., "Morphological and Mechanical Properties of Epoxy Foam Reinforced Composites", Society of Plastics Engineering (SPE) 2005 annual technical conference (ANTEC), Boston, Massachusetts, May 1-5 (2005)
12. Karaki, T., Sangari, S. S., Seferis, J. C., "Effects of particle modification on the fatigue damage progress in polynanömeric matrix composite laminates", Society of

Plastics Engineering (SPE) 2005 Annual Technical Conference (ANTEC), Boston, Massachusetts, May 1-5 (2005).

**Awards and Honors received by the PI (life-time received)**

Prof. Seferis was elected as an Honorary Member of the Greek Thermal Analysis Society after his opening keynote speech at the MEDICTA 2005 (7th Mediterranean Conference on Calorimetry and Thermal Analysis) on 2-6 July 2005 at Thessaloniki, Greece. His lecture titled "Polynanomeric Composites: A Novel Concept for Polymeric Composite Systems" utilized some of the thermal analysis data generated in this program.

**Transitions**

Prof. Seferis continued to work with his team of graduate students and a postdoctoral fellow, with industry and other academic institutions. Of interest was the application of the work through Mr. Terry L. Schneider of Material & Process Technology, Boeing Commercial Airplanes, as he was developing a shape memory alloy material base system for continuous fiber reinforces composites. Specifically, the adhesion of the metal particles to the matrix were addressed with our developing methodology in this program. This work will continue to transition into the next period as well. The work has also been transferred to the University of Delaware, Center for Composite Materials where Prof. Seferis has been a Research Professor since June 16, 2005.